

MOMENTUM DENSITY IN K_4C_{60} AND C_{60} M. MARANGOLO^a, F. QUÉRÉ^a, CH. BELLIN^a, G. LOUPIAS^{a,b}, J. MOSCOVICI^c, S. RABII^d,
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Abstract—Compton scattering measurements have been demonstrated to provide an accurate check of valence electron densities of solids, in the electronic ground-state. Experiments are carried out on powder samples of K_4C_{60} using 19.9 keV monochromatic beam provided by the synchrotron facility at LURE, Orsay. For comparison, C_{60} powder was measured in same experimental conditions.

A negative contribution in the momentum range [1,16] a.u. in the K_4C_{60} - C_{60} profile, which is impossible in a rigid-band approach, evidences the modifications of C_{60} valence electronic density in the K_4C_{60} compound.
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Among the K_nC_{60} compounds, K_4C_{60} exhibits particular behaviours. X-ray powder patterns tell us that its structure is a body centred tetragonal (bct) structure, in contrast to the other potassium intercalated phases that are all cubic [1].

Its isolant character has also intrigued the fullerene community: LDA band structure calculations [2] on the bct K_4C_{60} structure claim a metallic behaviour for this material and they are strongly at odds with the NMR and photoemission finding of an insulating ground state. Otherwise a good agreement with experimental data has been obtained by LDA calculations on C_{60} , K_3C_{60} and K_6C_{60} [3].

This K_4C_{60} anomaly led experimentalists to test the applicability of LDA approaches and of the quality of specific calculations. Compton scattering measurements can provide a direct experimental test of the ground state electronic density [4, 5] which, within LDA approximation, is related to the Fourier expansion of the one-electron wave functions.

Similar measurements have been carried out on solid C_{60} and graphite and an excellent agreement between measured electron momentum density and our LDA calculated Compton profiles was shown [6]. These results encouraged us to test K_nC_{60} band structure and, at the moment, we are able to compare K_4C_{60} and C_{60} Compton profile.

to a relationship between the energy lost by the photon and the projection of the initial electron momentum along the scattering vector \mathbf{K} . The component of this energy loss which results from scattering by the electrons at rest is referred to as the Compton shift. The motion of electrons in the system results in a Doppler broadening of the scattered photons energy distribution around the Compton shift and is a direct indicator of their initial momentum distribution [7-9]. In the case of valence electrons in solids, the scattering is commonly treated in the impulse approximation, where the scattering is assumed to be fast enough so that the same potential is observed by the electrons in their final as well as their initial state. In this approximation, the scattered photons spectrum is linked to the momentum distribution of electrons, as in the case of scattering by free electrons. It can therefore be used to determine the directional profile for the valence electrons, defined as:

$$J(q, \mathbf{e}) = \int n(\mathbf{p}) \delta(\mathbf{p} \cdot \mathbf{e} - q) d\mathbf{p} \\ \equiv \int \chi(\mathbf{p}) \chi^*(\mathbf{p}) \delta(\mathbf{p} \cdot \mathbf{e} - q) d\mathbf{p} \quad (1)$$

where $n(\mathbf{p})$ is the electron density obtained from the wave function $\chi(\mathbf{p})$. \mathbf{e} is the unit vector along the scattering direction and q is the projection of electron momentum \mathbf{p} on the unit vector \mathbf{e} .

1. COMPTON SCATTERING

Compton scattering involves the inelastic scattering of photons by electrons. When a photon is scattered by a free electron, the conservation of energy and momentum lead

2. EXPERIMENT PROCEDURES

The Compton profile of K_4C_{60} has been measured using a three axes focusing high resolution spectrometer [10]

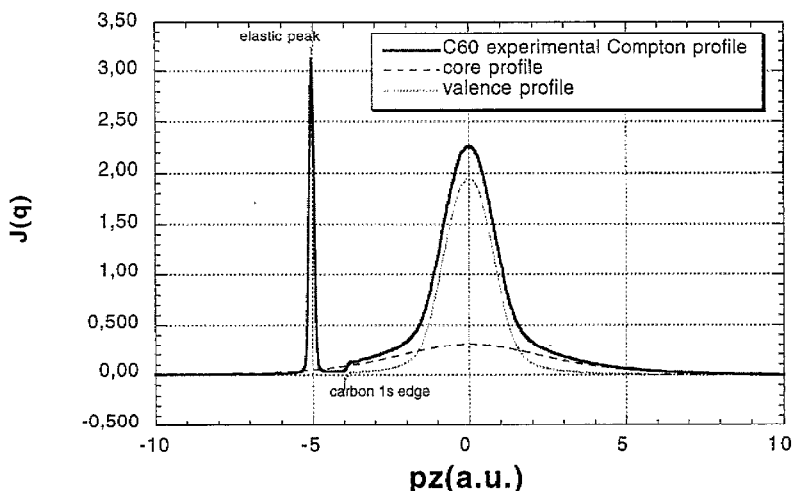


Fig. 1. Measured Compton profile for C_{60} . a) Total measured profile (—). b) Calculated core profile (---). c) Valence profile as difference between a) and b) (· · ·).

installed on the wiggler beam line at 'Laboratoire pour l'Utilisation du Rayonnement Électromagnétique' (LURE). The synchrotron radiation beam is monochromatised to select photons of 19.9 keV energy by Bragg reflection from a double crystal 111 silicon monochromator. The choice of the incident energy was made to fulfil the impulse approximation subject to the diminishing flux at increasing photon energy. The sagittal focusing of the incident beam [11], leads to a 5 mm spot on the sample. The photons are back-scattered by a sample of K_4C_{60} powder under argon atmosphere, energy analysed by means of a Si (440) Cauchois curved analysing crystal and focused to a single point on the Rowland circle. Here they are detected by a position sensitive detector which is situated tangentially to the focal circle. The detector is used to record the entire Compton spectrum at same time. The scattered photons spectrum is measured at the

scattering angle of 137° . The resolution is determined from the full width at half maximum of the thermal diffuse scattering peak, which is 0.2 a.u., when expressed in terms of the electron momentum scale.

For comparison, the Compton profile of a powder of C_{60} has been measured, using exactly the same experimental conditions as for K_4C_{60} . Difference of profiles obtained on the two solids is used in order to eliminate effects of systematic experimental errors.

3. DATA PROCESSING

After background subtraction, the raw data were corrected for the full energy-dependent terms [10] such as absorption in sample and analyser, detector efficiency and analyser reflectivity. The energy transfer (roughly 1 keV at Compton peak) is small enough for 1s electron

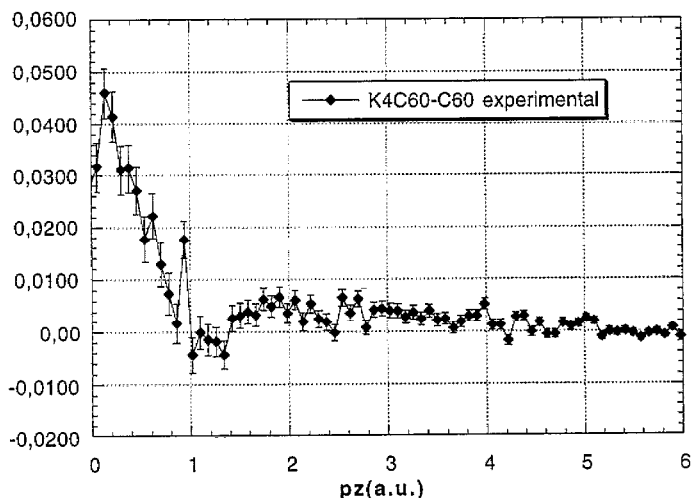


Fig. 2. Difference between ($K_4C_{60}-C_{60}$) and potassium core profile. The error bar is due to the statistical accuracy.

not to be involved in the process. The Impulse Approximation profiles of the core electrons of carbon and potassium have been subtracted to the total measured profiles: the C_{60} profile obtained in this way corresponds to the contribution of C_{60} valence electrons, and the K_4C_{60} profile is the sum of electrons initially 4s in potassium and electrons involved in the C_{60} molecule bonds.

All the valence profiles are normalised to the number of valence electrons per carbon atom, i.e. 4 in C_{60} profile and 4.47 in K_4C_{60} profile (carbon 2s, 2p and potassium 3p, 4s).

4. RESULTS AND DISCUSSION

Photon energy loss spectrum of C_{60} is shown in Fig. 1. The energy loss scale has to be converted into the momentum scale to obtain the Compton profile.

Fig. 2 shows difference profile $K_4C_{60}-C_{60}$ and potassium 3p atom profile, calculated within the Impulse Approximation. The difference profile is due to potassium insertion effects:

1. Charge transfer of the 4s K electron to C_{60} .
2. Presence of the initially 3p K electrons.
3. Distortion of the C_{60} electron density due to K^+ ions.
4. The structural transition (C_{60} cfc. \rightarrow K_4C_{60} bct).

Actually, the band calculations [3] of K_nC_{60} suggest that the 3p electrons are hybridised with any C_{60} valence bands.

This theoretical evidence encouraged us to subtract the atomic 3p electrons contribution from the total measured Compton profile. As a consequence, the electronic

modifications of C_{60} host can be due to both points 3 and 4. As shown in Fig. 2, the remarkable effect in the presented spectra is that the difference profile is negative in the momentum range [1, 1.6] a.u. Such a fact, which is impossible in a rigid-band approach, evidences the modifications of C_{60} valence electronic density in the K_4C_{60} compound

Ab initio self-consistent energy band calculations within local-density functional theory using the LCAO method with a Gaussian basis [2] are available. They will be used in the very next future in order to reconstruct the theoretical Compton profile [4]. Comparison between theoretical and measured Compton profiles will allow us to go to a deeper understanding of the role played by the inserted ionised potassium in C_{60} .

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